

CLAIMS

1. An engineered particle for an energy storage device, the engineered particle comprising:

an active material particle comprising an outer surface;

a conductive coating disposed on the outer surface of the active material particle, the conductive coating comprising a $M_xAl_ySi_zO_w$ film; and

at least one carbon particle disposed within the conductive coating,

wherein **M** is an alkali selected from the group consisting of Na and Li, and $1 \leq x \leq 4$, $0 \leq y \leq 1$, $1 \leq z \leq 2$, and $3 \leq w \leq 6$.

2. The engineered particle according to claim 1, wherein the $M_xAl_ySi_zO_w$ film has an alkali ion conductivity of about 10^{-5} S/cm.

3. The engineered particle according to claim 1, wherein the $M_xAl_ySi_zO_w$ film is amorphous.

4. The engineered particle according to claim 1, wherein the active material particle has a size within a range of about 0.01 μm to about 50 μm .

5. The engineered particle according to claim 1, wherein the active material particle comprises at least one material selected from the group consisting of a lithium intercalating particle and a sodium intercalating particle.

6. The engineered particle according to claim 1, wherein the active material particle comprises at least one material selected from the group consisting of:

a lithium intercalating material selected from the group consisting of LiCoO_2 , LiNiCoAlO_2 , LiNiMnCoO_2 , LiFePO_4 , LiMnO_2 , SnO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, graphite, SiO_2 , sulfur, graphene oxide, and activated carbon;

a sodium intercalating material selected from the group consisting of NaCoO_2 , NaNiCoAlO_2 , NaNiMnCoO_2 , NaFePO_4 , NaMnO_2 , $\text{Na}_4\text{Ti}_5\text{O}_{12}$, sulfur, graphite, graphene oxide, and activated carbon; and

a non-sodium or non-lithium containing material selected from the group consisting of graphite, sulfur, activated carbon, graphene oxide, SiO_2 , or SnO_2 .

7. A secondary battery comprising:

a cathode;

an anode; and

an electrolyte,

wherein at least one of the cathode and the anode comprises the engineered particle of claim 1.

8. A method of fabricating a cathode for an alkali-ion battery, comprising the steps of:

a) forming coated particles by:

forming particles of an alkali-intercalating material;

mixing said particles of the alkali-intercalating material with an aqueous solution comprising an aluminum salt and an alkali metal salt to form a first slurry;

adding a water-soluble alkali silicate into said first slurry;

adding electrically-conductive carbon nanoparticles into said first slurry;

sonicating said first slurry to produce a gel;

drying said first slurry to form individual dry green coated gel particles; and,

heat treating said green coated gel particles to produce coated particles comprising said particles of the alkali-intercalating material, a conductive coating comprising an alkali aluminosilicate, and carbon nanoparticles disposed within the conductive coating;

b) blending said coated particles with conductive particles, an organic binder, and at least one non-aqueous solvent to form a second slurry;

c) applying a coating of said second slurry to a metal substrate with said substrate heated between 80 and 200°C in air;

d) calendaring said coated substrate at 10 tons or greater;

e) curing the coated substrate in nitrogen at 250 to 400°C.

9. The method of claim 8, wherein said conductive coating comprises a $M_xAl_ySi_zO_w$ film and at least one particulate material selected from the group consisting of: a carbon particle, a graphene particle, and a carbon nanotube particle, said particulate material disposed within the conductive coating, and wherein **M** is an alkali selected from the group consisting of Na and Li, and $1 \leq x \leq 4$, $0 \leq y \leq 1$, $1 \leq z \leq 2$, and $3 \leq w \leq 6$.

10. The method of claim 8, wherein said aqueous solution comprises $Al(NO_3)_3$ and at least one salt selected from the group consisting of $LiNO_3$ and $NaNO_3$.

11. The method of claim 8, wherein said water-soluble alkali silicate is selected from the group consisting of a lithium silicate solution and a sodium silicate solution.

12. The method of claim 8, wherein said electrically-conductive carbon nanoparticles are selected from the group consisting of carbon black, graphene, carbon nanotubes, and combinations thereof.

13. The method of claim 8, wherein said step of heat treating said green coated particles comprises curing at about 300°C followed by annealing at 400 to 600°C in an atmosphere selected from the group consisting of nitrogen, argon gas, and combinations thereof.

14. The method of claim 8, wherein applying said coating comprises a slot coating method.

15. The method of claim 8, wherein applying said coating comprises a spray coating method and said second slurry comprises 25 to 50 mL of at least one non-aqueous solvent per 2 g of solids.

16. An alkali-ion energy storage device comprising:
a cathode;
an anode;
a separator; and,

an aqueous electrolyte,
wherein at least one of said cathode and said anode comprises the engineered particle of claim 1.

17. The energy storage device of claim 16,
wherein said cathode comprises:
a first particulate material selected from the group consisting of NaMnO_2 and LiMnO_2 ;
a second particulate material selected from the group consisting of conductive carbon particles and carbon nanotubes; and,
PVDF binder;
wherein said anode comprises
a third particulate material selected from the group consisting of activated carbon, graphene oxide, conductive carbon particles, and carbon nanotubes; and,
PVDF binder;
wherein said separator comprises a cotton cloth; and,
wherein said aqueous electrolyte comprises a solution of at least one species selected from the group consisting of LiNO_3 , Li_2SO_4 , NaNO_3 , and Na_2SO_4 .

18. The energy storage device of claim 16, wherein said device is selected from a group consisting of a battery and a capacitor.

19. An alkali-ion energy storage device comprising:
a cathode;
an anode;
a separator; and,
a non-aqueous electrolyte;
wherein at least one of said cathode and said anode comprises the engineered particle of claim 1.

20. The energy storage device of claim 19,
wherein said cathode comprises

a first particulate material selected from the group consisting of: LiNiMnCoO_2 and NaFePO_4 ;

a second particulate material selected from the group consisting of: conductive carbon particles and carbon nanotubes; and,

PVDF binder;

wherein said anode comprises

a third particulate material selected from the group consisting of: graphite, conductive carbon particles, activated carbon, graphene oxide, graphene, and carbon nanotubes; and, PVDF binder; or

Li or Na foil protected by particulate material selected from SnO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, graphite, or SiO_2 ,

wherein said separator comprises a porous polymeric membrane; and,

wherein said non-aqueous electrolyte comprises from the group consisting of LiPF_6 dissolved in ethyl carbonate/ethyl methyl carbonate, NaPF_6 dissolved in ethyl carbonate/ethyl methyl carbonate, LiFSI dissolved in ethyl carbonate/ethyl methyl carbonate, NaFSI dissolved in ethyl carbonate/ethyl methyl carbonate, and ionic liquids.

21. The energy storage device of claim 19, wherein said device is selected from a group consisting of a battery and a capacitor.

22. A method for making a stabilized Li anode for high energy density Li batteries of claim 19 comprising the steps of:

a) forming coated particles by

forming particles of a lithium-intercalating material;

mixing said particles of the lithium-intercalating material with an aqueous solution comprising an aluminum salt and a lithium metal salt to form a first slurry;

adding a water-soluble lithium silicate into said first slurry;

adding electrically-conductive carbon nanoparticles into said first slurry;

sonicating said first slurry to produce a gel;

drying said first slurry to form individual dry green coated gel particles; and,

heat treating said green coated gel particles to produce coated particles comprising said particles of the lithium-intercalating material, a conductive coating

- comprising a lithium aluminosilicate, and carbon nanoparticles disposed within the conductive coating;
- b) providing a metal current collector;
- c) coating said metal current collector with Li metal;
- d) spray coating said Li-coated metal current collector with a second slurry containing said coated particles, a non-aqueous solvent, and conductive particles; and
- e) curing said spray-coated metal current collector at 100 to 300°C.

23. The method of claim 22, wherein said metal current collector is selected from the group consisting of a foil or a mesh.

24. The method of claim 22, wherein said metal current collector is selected from the group consisting of copper, nickel, and stainless steel.

25. The method of claim 22, wherein coating said metal current collector comprises forming a coating of Li metal said metal current collector by method selected from the group of evaporation of Li metal and laminating with Li metal foil.

26. The method of claim 22, wherein said non-aqueous solvent is selected from the group consisting of hexane, toluene, and benzene.

27. The method of claim 22, wherein said conductive particles comprise conductive carbon.

28. The method of claim 22, wherein said second slurry further comprises particles selected from the group consisting of engineered SnO₂ particles, engineered Li₄Ti₅O₁₂ particles, engineered graphene oxide particles, and engineered SiO₂ particles.